

Use of Humic Substances to Remediate Polluted Environments: From Theory to Practice

Edited by

Irina V. Perminova, Kirk Hatfield and
Norbert Hertkorn

NATO Science Series

Use of Humic Substances to Remediate
Polluted Environments:
From Theory to Practice

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Use of Humic Substances to Remediate Polluted Environments: From Theory to Practice

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Printed in the Netherlands.

This volume is dedicated to **Galina Moiseevna Varshal** – the prominent Soviet-Russian scientist, Professor of the Institute of Geochemistry and Analytical Chemistry (GEOKHI) of the Russian Academy of Sciences.

She passed away on July 16, 2001; her lecture on the geochemical role of humics in metal migration was to open the Workshop.

Galina M. Varshal was an outstanding scientist and a bright and generous person. This volume is dedicated to Galina Moiseevna in appreciation for her devoted service to the science of humic substances.

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PREFACE

Effective remediation of polluted environments is a priority in both Eastern and Western countries. In the U.S. and Europe, remediation costs generally exceed the net economic value of the land. As a result, scientists and engineers on both sides of the Atlantic have aggressively tried to develop novel technologies to meet regulatory standards at a fraction of the costs. *In situ* remediation shows considerable promise from both technical and economic perspectives. *In situ* technologies that deploy natural attenuating agents such as humic substances (HS) may be even more cost effective. Numerous studies have shown humics capable of altering both the chemical and the physical speciation of the ecotoxicants and in turn attenuate potential adverse environmental repercussions. Furthermore, the reserves of inexpensive humic materials are immense. Which suggests HS portend great promise as inexpensive amendments to mitigate the environmental impacts of ecotoxicants and as active agents in remediation.

To elucidate emerging concepts of humics-based remediation technologies, we organized the NATO Advanced Research Workshop (ARW), entitled "Use of humates to remediate polluted environments: from theory to practice", held on September 23-29, 2002 in Zvenigorod, Russia (see the web-site <http://www.mgumus.chem.msu.ru/arw>). The purpose of this ARW was to bring for the first time a league of experienced scientists who have studied humics structures, properties and functions in the environment, together with an association of environmental engineers who have developed novel remediation technologies. The workshop created among the participants an awareness of the current status of research in remediation chemistry and in humics technology. At the meeting, 20 oral and 29 poster presentations were given followed up by multiple discussions that were both engaging and constructive.

This book summarizes the proceedings of the Workshop, and is dedicated to Professor G.M. Varshal (deceased). Four chapters appearing in this volume are from authors who could not attend the workshop, but kindly agreed to prepare written contributions (J.F. De Kreuk, J.A. Field, D.S. Gamble, and V. Moulin). Three reports from Working Group discussions prepared by rapporteurs designated at the ARW are included in the Introduction. All papers have been subject to peer review by at least two referees. We thank all the authors for their helpful collaboration.

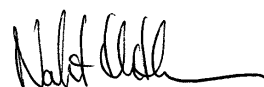
We are grateful for the financial support from NATO Science Affairs Division, which made it feasible to organize this Workshop. We thank Muefit Tarhan (Humintech Ltd.) for the monetary awards to the best poster presenters. The hard work of Joy Drohan (Eco-Write) on editing the translations from Russian is deeply acknowledged. We also wish to express our sincere appreciation to Dr. Natalya A. Kulikova and Alexey V. Kudryavtsev for their invaluable assistance in organizing the Workshop and in preparing this volume for publishing.



Irina V. Perminova



Kirk Hatfield



Norbert Hertkorn

INTRODUCTION

1. Objectives of the book

The aim of this book is to establish a linkage between scientists who have studied humics structures, properties and functions in the environment, and environmental engineers who have developed novel remediation technologies. In pursuing this goal, the engineer interested in remediation is provided with sufficient information on the basics and state-of-art of humics research pertinent to remediation. On the other hand, for the interested scientist familiar with the basic research on humics, this text provides sufficient information on the methods, needs, and limitations of existing remediation technologies, and on the latest developments in applied humic research. It is the objective of the authors that this text be sufficiently thorough that it serves to facilitate the development of a common language and stimulate discussions among scientists and engineers. The diverse expertise brought together to create this book promises desirable synergetic effects of solving remediation problems by revealing new fields of applied humic research and extending current technical application of humics.

The principal objective of the book is to elaborate a systematic characterization of the mediating effects of HS by categorizing these effects according to their impact on the fate of ecotoxicants and on the physiological functions of living organisms. Given the subtitle: 'from theory to practice', another substantial objective is to assess the status of knowledge pertaining to the function or role humics may serve in the remediation of polluted environments, and to show the limits of current knowledge on the properties and functions of HS. Concerning the practice of remediation, principal objectives are to assess the scope of current applications, to define promising directions of technological developments, and to formulate the research needs. Hence, the volume pays particular attention to *in situ* remediation technologies as the most viable option for the application of humics as active agents in remediation.

2. Organization of the book

This book contains 24 chapters that are structured into five parts. Part 1 gives a general overview of the remedial properties of humic substances and identifies various challenges pertinent to their application in remediation. The first part also introduces the topics of subsequent sections. For example, the focus of Part 2 is the interaction that occurs between HS and heavy metal and radionuclide via complexation. Part 3 addresses sorption/partitioning as a primary interaction between humics and organic ecotoxicants. Then there is Part 4, where the topic is humics interactions with the physiological functions of living organisms and their effects on microbially mediated ecotoxicant transformations. Finally, in Part 5 analytical approaches for quantifying HS

structure and properties are discussed, as are studies where humic materials have been modified to acquire desired properties.

2.1. REMEDIAL PROPERTIES OF HUMIC SUBSTANCES: GENERAL CONSIDERATIONS AND PROBLEMS IN ADDRESSING NEEDS OF ENVIRONMENTAL REMEDIATION

The first chapter gives a general introduction to the field of remediation chemistry in context of humic substances potential implications. It provides an overview of the interactions encountered between HS, ecotoxins, and living organisms in a polluted environment. The most important interactions identified include: binding interactions affecting chemical speciation and bioavailability of contaminants; interfacial interactions altering physical speciation or interphase partitioning of ecotoxins; abiotic-biotic redox interactions that influence metabolic pathways coupled to pollutants; and finally direct and indirect interactions coupled to various physiological functions of living organisms. All of these interactions possess significant utility for *in situ* remediation; consequently, several humic-based reactions are examined in detail that are pertinent to permeable reactive barriers, *in situ* flushing, bioremediation, and phytoremediation. Finally, this chapter introduces the novel concept of “designer humics” which are a special class of customized humics obtained by chemically modifying and cross-linking the humic backbone such that this new humic-based material acquires specified reactive properties. Designer humics, as described herein possess the potential for achieving enhanced remediation and for quantifying remediation performance. The latter is described in the context of the passive flux meter technology.

Chapter 2 presents the general theory of humification, describes the biogeochemical rules of humus formation in soil, and defines the functions of HS in the biosphere. The kinetic nature of humification process is given particular consideration. The following features inherent to the process of forming humus are identified: first, the process is biomineral in nature; second, transformations of organic matter are biothermodynamically driven; and third, the quality of humus generated is determined by the prevailing environmental condition at each stage of humification. Chapter 2 defines five principal functions displayed by HS in the biosphere; these are the accumulative, transport, regulatory, physiological and protective functions. The protective function is considered in detail. Experimental evidence is provided for the example of interactions occurring between soil humics and heavy metals.

Chapter 3 sets the stage for improvements the quantitative prediction of reaction equilibrium between HS and different reagents. The reviewed literature clearly shows that the principles of classical chemistry, as understood for monomeric reagents, are to some extent adaptable to humic complex mixtures. Demonstrations of predictive chemical calculations have been published and the practical implications are discussed herein. However, this chapter emphasizes that there is an urgent need for a new generation of models (perhaps stochastic in formulation) capable of predicting the reactive properties of humics. These new models will play a crucial role in the design of novel humics-based remediation strategies.

2.2. COMPLEXING INTERACTIONS OF HUMIC SUBSTANCES WITH HEAVY METALS AND RADIONUCLIDES AND THEIR REMEDIAL IMPLEMENTATION

The topic of humics/heavy metals interactions is developed in Chapter 4. Authors provide the requisite theoretical background and review data on the complexing capacity of humics for various heavy metals. The role of HS interactions in metal uptake by higher plants is given particular attention. Impacts of HS on heavy metal speciation, migration, and toxicity in aquatic environments are discussed in Chapters 5 and 6. The former focuses on changes in the complexing properties of UV-oxidized natural organic matter (NOM). It is shown that UV oxidation reduces the molecular size of the NOM and in turn decreases its inherent Al-complexing capacity. Of interest is that UV-oxidation does not effect the same change in the complexing properties of NOM towards Pb and Zn. Relationships between the structure and the complexing properties of NOM are further addressed in Chapter 5. Studies of seasonal variations evident in the properties of NOM in the natural waters reveal significant decreases in complexing capacity in late spring and early summer, when NOM is enriched with the newly produced organic matter. In this context of particular importance is the demonstrated coupling between NOM complexation with ecotoxicants and the resultant detoxification. Model systems with copper show that a decrease in water toxicity is correlated with a reduction in the concentration of free metal produced when copper binds to NOM. The given results elucidate a coupled relationship between the structure of humics and their ability to complex heavy metals.

Chapter 7 reviews a vast pool of data on HS interactions with the most dangerous metal contaminants, radionuclides. The data originates from research conducted at the Centre of Atomic Energy (CEA) in France. The chapter provides a solid analytical background of investigations focused on the complexing properties of HS with radionuclides. Data on the stoichiometry of the complexes and the respective stability constants are given for actinides, iodine and lanthanides. Results presented are obtained for Aldrich humic acid, and aquatic fulvic acid. Discussed is the influence HS have on the retention of trace element on mineral surfaces. The latter topic is the focus of Chapter 8 where HS are considered as components of geochemical barriers for actinide migration. Original results on sorptive and redox interactions in a mineral-HS-actinide system are given. A conclusion is drawn regarding the suitability of using humics as agents to immobilize actinides in contaminated environments. This conclusion is confirmed by results of a case study presented in Chapter 9. Both laboratory and field studies demonstrate that treating polluted soils with brown coal composed of up to 80% humic acids induces a drastic reduction in the mobility and toxicity of heavy metals. This shows that humic materials can be used to ameliorate heavy metals toxicity in soils.

In summary, the above chapters clearly demonstrate HS can affect metal speciation and migration in soil and aquatic environments. The structure features found in the humic macromolecule are of particular importance when assessing the binding affinity for metals. The more oxidized, low molecular weight humics (i.e., fulvic acids) produce less stable and more mobile complexes; whereas, the less oxidized and higher molecular weight humics (i.e., humic acids) produce more stable and less mobile complexes. Hence, humic acids function as both detoxifying and binding agents; whereas fulvic

acids may be more effective as flushing agents useful for remediation metal contaminated soils and aquifers.

2.3. SORPTIVE-PARTITIONING INTERACTIONS OF HUMIC SUBSTANCES WITH ORGANIC ECOTOXICANTS AND THEIR REMEDIAL IMPLEMENTATION

Chapter 10 is devoted to examining the sorptive interactions of HS with minerals and with organic contaminants and to discussing the prospects of their use in permeable reactive barrier (PRB) technologies. Basic concepts are addressed relevant to the *in situ* remediation of hydrophobic organic contaminants (HOC) contaminated aquifers using sorptive PRBs. Particular attention is given to an original concept of creating an *in situ* sorptive PRB through a sequential process of first coating aquifer materials with an iron precipitate that is then covered with humics. The obtained humic coating induces sorptive interactions with dissolved HOC, and thus, retards their migration. The results of significant laboratory experiments are given. A design of a corresponding field experiment is discussed. The considerations given thus far on the sorptive interactions of humic coatings with HOC and on the use of humics in sorptive PRBs are complemented by the contents of Chapter 11. This chapter examines the partitioning interactions between humics and HOC in the framework of using concentrated humic solutions as flushing agents for the remediation of polluted aquifers. Colloidal dispersions of HS are shown to enhance the removal of HOC from aquifers. It is clearly demonstrated that a concentrated solution of Aldrich® humic acid can be used to flush diesel fuel from a pilot-scale model sand aquifer. Experiment shows elevated organic constituent solubility producing an accelerated rate of plume remediation. Practical recommendations on a use of HS as flushing agents are given.

Chapter 12 complements considerations given to the use of HS as flushing agents by identifying problems of soil bioremediation caused by the mass transfer limitations. Several factors are identified as constraining the performance of bioremediation in the field including: the groundwater flow rate; the soil structure heterogeneity; the binding of contaminants to organic matter; the binding of essential nutrients to soil; and the presence of contaminants in an immiscible phase (i.e., DNAPL). The chapter concludes with a proposed strategy of using concentrated humic solutions to facilitate groundwater flow through hydrophobic zones of contaminated aquifer. With nutrients and electron donors/acceptors supplied, local indigenous microorganisms are stimulated to degrade contaminants, and bioremediation resumes. Chapter 13 introduces another feasible strategy of using the interfacial activity of HS to meet the needs of *in situ* remediation. This chapter describes an original approach to improving the biodegradability of organic contaminants in wastewaters using cationic surfactant modified zeolites. Zeolite particles are good carriers of bacteria, but the formation of the bacteria layer on the zeolite surface is slow. The approach requires the attachment of cationic surfactants to the surfaces of zeolite particles. The sorbed polyelectrolytes alter the surface charge on the zeolite particles which in turn accelerates the surface sorption of bacteria. The resultant increase in sludge density produces a desirable increase in sludge activity. The efficiency of

modified zeolites has been proven in the laboratory and in full-scale experiments. Use of HS for modification of zeolites as an alternative to artificial surfactants is discussed.

In summary, it can be concluded that when fixed on mineral surfaces, HS can retard the migration of organic contaminants, and when dissolved in water, humics can facilitate the transport of the contaminants in the subsurface. The former process heralds opportunities to use humics as sorbents in PRB, while the latter process is of particular value where humics can function as reactive agents in flushing technologies and in bioremediation.

2.4. IMPACT ON PHYSIOLOGICAL FUNCTIONS OF LIVING ORGANISMS AND ON MICROBIAL TRANSFORMATIONS OF ECOTOXICANTS

Chapter 14 presents a broad overview of the mitigating effects exerted by HS over living organisms in the polluted environments. Several major pathways of mitigation are identified including, impacts on organism development (as an organic carbon source and as hormone-like compounds), impacts on nutrient transport across cell membranes, interactions with enzymes including impacts on biochemical reactions, and finally, antioxidant activity. The original data on enhanced transport of nutrients and on hormone-like and antioxidant activity are presented. Chapter 15 introduces original concepts of how humics impact cell physiology. It is based on the assumption that the physiological interactions of interest occur after HS have crossed the cell membrane and are engaged in particular metabolic activities, such as protein synthesis. This precludes any damage to the system responsible for protein synthesis that might otherwise result from negative environmental factors. Given the critical role of protein synthesis when cells adapt to unfavourable conditions, HS are considered natural adaptogens. Experimental results are given on the adaptogenic activity of HS.

In Chapter 16 the focus is on humic interactions that provide stability to extracellular enzymes in the soils. Presented is a vast pool of experimental data on HS induced protease inhibition in the presence of different metals. It is shown that humics are non-specific inhibitors of proteases, and that metals, possessing a higher binding affinity for HS, exhibit a pronounced effect on the stability of enzyme-HS complexes.

The multiple roles of HS in redox reactions catalysed by various microorganisms are considered in Chapter 17. HS are ascribed to have three distinct roles as electron carriers that support biotransformation of priority pollutants, nominally, as electron acceptors for respiration; as redox mediators for reduction processes; and as electron donors to microorganisms. The evidence provided in this review indicates that humics can stimulate the anaerobic (bio)transformation of a wide variety of organic and inorganic compounds, including priority pollutants. Chapter 18 presents a practical example of a bioremediation technology based on the ability of HS to participate in microbial redox reactions. The corresponding technology was developed for the remediation of soil and water sites polluted with explosives (2,4,6 trinitrotoluene, TNT). In reducing environments TNT was reduced to amino-metabolites that produced bound residues with soil organic matter. The experiments were performed on a pilot-scale and in the field. Best results were obtained using molasses as the source of organic carbon for

biological reduction. The technical feasibility using this bioremediation strategy at sites contaminated with explosives was clearly demonstrated.

Chapters 19 and 20 present studies of the impacts of commercial humates on soil properties and higher plant development under conditions where heavy metals, radionuclides, and herbicides are the primary pollutants. Chapter 19 reports on the mitigating actions of humates extracted from coal and peat obtained both in the lab and the field. Conclusions are formulated on the prospects of using humics to detoxifying polluted soils and particularly, for the case of combined pollution. Chapter 20 describes application of three commercial humates produced by the same company as adjuvants of the polluted soil. The structure and soil amending properties of all three humate samples studied were quantified. Conclusions were drawn on substantial structural differences between the humate samples studied. Of particular interest was that two structurally similar humates exerted different stimulating effects on plant growth. The results obtained demonstrate that only under standardized production schemes it is possible to produce humic materials of predictable quality.

2.5. QUANTIFYING STRUCTURE AND PROPERTIES OF HUMIC SUBSTANCES AND EXAMPLE STUDIES ON THE DESIGN OF HUMIC MATERIALS OF THE DESIRED PROPERTIES.

Chapter 21 and 22 are devoted to describing the use of high-resolution analytical techniques such as nuclear magnetic resonance (NMR) spectroscopy and capillary zone electrophoresis (CZE) for the investigation of humic structures and of humic interactions with contaminants. These Chapters are complementary with respect to the topics and data discussed. The NMR-spectroscopy approach presented in Chapter 21 gives detailed chemical information on structural components; whereas, the CZE provides information on the molecular behaviour of HS in solution. By defining the relative amounts and structural details of fundamental building blocks, multinuclear quantitative one-dimensional NMR spectroscopy provides the key margin of any structural model of NOM/HS. A large array of higher dimensional NMR spectra permits improved definition beyond the extended substructures of NOM/HS. CZE primarily offers information on the charge, conformation, and charge density of HS; all of which are important parameters when investigating their interactions with pollutants. A detailed description of CZE separation processes is given to interpret the behaviour of humics in aqueous media. Based on the numerous measurements of different HS samples, the conclusion is drawn that humics in aqueous solutions behave as molecular associates showing a distribution of the electrophoretic mobilities in the anionic range. CZE offers a quantitative description of the charge density distribution among the molecular associates. The aspects of structural dynamics are essential for modelling humic-pollutant interactions.

Chapters 23 and 24 address the problem of producing humic materials of desired quality using a novel approach of directed chemical modification. The presented direction can be considered a significant shift in HS-related research, because previous investigations involving humic modifications were focused on developing an understanding of humics structure, not to enhance or change reactive properties.

Chapters describe ozonation and sulfonation as two methods of introducing functional groups into humics derived from coal and peat. Sulfonation increases the solubility of humic-metal complexes, whereas ozonation enriches HS with hydroxyl groups of enhanced chelating ability. An examination of the metal-complexing properties of sulfonated derivatives comply well with desired changes in the properties of the parent humics. It was concluded that chemical modification holds considerable promise as a means of producing humics of the desired properties.

Concluding on the papers overview, two fundamental reasons can be cited as to why HS have not been widely used in remediation technologies. First, few natural HS possess the specific reactive properties required to treat selected environmental contaminants. Second, humics are by definition polydisperse and heterogeneous; consequently, their reactive properties vary between natural sources and between industrial suppliers. Lacking the specificity of action, HS can be referred to as low efficient adjuvants. In addition, because humics possess an ill-defined structure, their properties are difficult to predict. It is believed that the nature and the quality of humics need to be assessed quantitatively, and that such an assessment could facilitate the prediction of humic properties. Improving tools to predict humic properties, and in addition, developing the novel concept of the producing humic materials of the desired properties, portend new opportunities for the broader application of humic-based products in the field of environmental remediation.

3. Outcomes of the round-table discussions: From practice to theory?

Outcomes of the round-table discussions reflected the findings and conclusions of three working groups (WG). Discussion topics were chosen in support of the main task of the workshop and each focused on the application of humics in remediation. The topic of WG 1 was "Humics as binding agents and detoxicants", for WG 2 "Humics as sorbents and flushing agents", and for WG 3 "Humics as biologically active substances". The outcomes of each WG were summarized below.

3.1. FINDINGS OF WORKING GROUP ONE: "HUMICS AS BINDING AGENTS AND DETOXICANTS" (RAPORTEURS: F.H. FRIMMEL, I.V. PERMINOVA)

This working group examined first the question of how best to use the binding properties of HS as a tool or function in remediation. The binding functions considered included:

- a) Detoxification by complexation (reversible binding, mostly metals);
- b) Detoxification by incorporation into humics structure (irreversible covalent binding of organic contaminants);
- c) Intelligent mobilization (binding/release): to have humics function at the correct place and at the opportune moment as scavengers for metals and other contaminants (recycling technology), and as carriers for nutrients (bioremediation technologies).

The working group next sought to determine what is not known, or what is needed to characterize the binding properties of HS in such a fashion that their function in the polluted environment becomes predictable. The issues and concerns raised included:

- a) Can we define the reactive properties of humics that are consistent with the needs of various remediation technologies?
- b) Can we predict these remedial properties of humics?
- c) Can we quantify the key remedial properties of humics?
- d) Do we have the tools to control the remedial properties for producing humics with predictable reactive properties suitable for a certain remediation technology?

The answers to the above issues and concerns were:

- a) A specific knowledge is lacking on the remedial properties of HS; while, the requisite systematic studies are missing.
- b) Quantitative structure-property relationship (QSPR) approach is a promising tool for predicting the remedial properties of HS. To make it work, we need to develop consistent descriptors (parameters) of the remedial properties.
- c) We need appropriate analytical techniques and data treatment tools to measure these parameters and predict the properties.
- d) Directed chemical modification could be a promising tool for producing humics with the desired remedial properties.

Conclusions: If the above issues and concerns were addressed in a way that key humic properties pertinent to remediation could be defined, and that the descriptors/parameters of these properties and the techniques to assess them could be developed, then humics of appropriate properties could be match to a given remediation problem. Moreover, new humic materials could be tailored or designed to possess properties suitable for remediation.

3.2. FINDINGS OF WORKING GROUP TWO: "HUMICS AS SORBENTS AND FLUSHING AGENTS" (RAPPORTEUR: G.U. BALCKE)

This working group sought to identify how the sorptive properties of HS could be used to immobilize or mobilize contaminants from an engineering perspective.

The group proposed a general list of actors involved in mobilization/immobilization technologies. This list included both contaminants: metals; organometallics; organics; and humics: humic preparations; humics-containing and humics-derived materials.

Where HS could be used for immobilization, the contaminants of interest included:

- a) Heavy metals; radionuclides; metal oxoforms.
- b) Polychlorinated and polycyclic aromatic compounds.
- c) Pesticides, dyes, anilines, etc.

Where humics could be used for mobilization, the identified contaminants were:

- a) Moderately hydrophobic compounds such as naphthalene.

The working group proposed potential areas where humics could be applied to address environmental problems including:

- a) Pollution prevention: for example, a landfill liner;
- b) Environmental remediation (flushing/immobilization applications): contaminant retardation (immobilization); contaminant mobilization (flushing); reactant retardation (*in situ* PRB construction).

Finally, the working group formulated a list of the advantages and limitations of using humics for mobilization/immobilization based remediation strategies.

The perceived advantages were:

- a) Humics are cost effective because 1) different production processes produce a large available supply of humics-containing waste, 2) there exist enormous reserves of raw humics, and 3) humics can be recycled.
- b) Humics are generally soluble and thus easily introduced into the subsurface.
- c) Humics are environmentally friendly (non-toxic).
- d) Humics are environmentally recalcitrant (non-biodegradable).
- e) Some reactions with contaminants are irreversible.

The identified disadvantages/limitations included:

- a) Unknown stability of humics-contaminant complexes (feasible release of the contaminant due to dissociation of the formed complexes).
- b) Plugging of the porous media due to uncontrolled humic precipitation.

Conclusions: The working group surmised that humics could be used to facilitate both contaminant mobilization and immobilization. Responsible use, however, requires that sorption be treated as a reversible process. This means that contaminant release or remobilization is feasible and must be considered in an assessment of risks associated with the remediation. Finally, long-term studies of the performance of humic sorbents and flushing agents are needed under a broad range of environmental conditions.

3.3. FINDINGS OF WORKING GROUP THREE: "HUMICS AS BIOLOGICALLY ACTIVE SUBSTANCES" (RAPPORTEUR: O.V. KOROLEVA)

The third working group examined first, humic functions pertinent to *in situ* bioremediation. Particular attention was given to functions which facilitate long-term stability within the subsurface microbial consortia. The functions examined were:

- a) Protective (detoxifying).
- b) Transporting (carrier of metals: sorption/desorption and distribution among the microorganisms of a consortium).
- c) Stabilizing (immobilization of enzymes or microbes on the minerals resulting in better growth, and enhancing metabolic reactions of methanogenic, nitrifiers, cellulolytic, lignolytic, and other microorganisms).
- d) Nutritional (bacteria are able to utilize the low molecular weight compounds formed as a result of irradiation of humics; the similar compounds are formed during the growth of some fungi, e.g. basidiomycetes).

Next, the working group sought to determine what is not known or what is needed to assess and to predict humic functions coupled to biological activity. The issues examined were:

- a) Can we define the biochemical functions of HS if their synthesis has no genetic code?
- b) What is an appropriate approach to assess biological activity of humics?
- c) Can we define the biological effects pertinent to bioremediation?
- d) How can we characterize the desired biological effects of humics?
- e) How can we quantify biological activity of HS?

The answers obtained to the above issues and concerns were:

- a) General biological terms can be applied to characterize the biological activity of humic substances.
- b) The most promising approach leading to a comprehensive assessment of biological activity is a hierarchical evaluation (from molecule to organism, from organism to ecosystem) of biological effects on living organisms.
- c) A broad array of the bioassays should be applied for defining the biological effects of HS, e.g. in case of HS interaction with plant cells, the following processes should be monitored: sorption onto a cell membrane, changes in the Na/K balance, and changes in the Ca/Mg ratio of cell membrane transport.
- d) The bioassays should be performed under standardized conditions ensuring observation of the direct impact of HS on the organisms, and not of their indirect impact due to interactions with components of cultivation media; the studies for determining and standardizing such conditions for bioassays are needed.
- e) Ranking could be a desirable quantitative tool for assessing parameters of biological activity from results of different bioassays.

Conclusions: The working group surmised that humics could be used for bioremediation to ensure the long-term stability of microbial consortia. Efficient use, however, requires humic materials exhibiting effects that are substantially beneficial to the microbial consortia. Comprehensive studies of the biological activity coupled to HS are needed that would examine the various biological effects at each organizational level (molecules, organelles, cells, etc.) using a broad array of bioassays. Clearly, standardization of these bioassays is needed.

3.4. SUMMARY OF THE ROUND TABLE DISCUSSIONS

From both theoretical and practical perspectives, the above findings of the working groups clearly disclosed gaps in existing knowledge and simultaneously defined future research needs. The summary of shortcomings evident in current humics research was perfectly complemented with the substantial comments from remedial engineers (Thomas and Dias). They gave an overview of practical demands and needs in the context of the knowledge gained on the properties and potential uses of humics. This contribution inspired vivid discussions; furthermore, it motivated participants to consider a follow-up workshop with a working theme of "use of humics to remediate polluted environments: from practice to theory." The proposed workshop would focus on the limitations of remedial practices and would reveal novel opportunities for the use of humics in solving those problems.

The Editors

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Part 1

Remedial properties of humic substances:
general considerations and problems
in addressing needs of environmental remediation

REMEDICATION CHEMISTRY OF HUMIC SUBSTANCES: THEORY AND IMPLICATIONS FOR TECHNOLOGY

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Abstract

An overview is given of the interactions encountered between humic substances (HS), ecotoxicants, and living organisms in the context of environmental remediation. The most important interactions identified include: binding interactions affecting chemical speciation and bioavailability of contaminants; interfacial interactions altering physical speciation or interphase partitioning of ecotoxicants; abiotic-biotic redox interactions that influence metabolic pathways coupled to pollutants; and finally direct and indirect interactions coupled to various physiological functions of living organisms. Because humics are polyfunctional, they can operate as binding agents and detoxicants, sorbents and flushing agents, redox mediators of abiotic and biotic reactions, nutrient carriers, bioadaptogens, and growth-stimulators. It is shown that these functions possess significant utility in the remediation of contaminated environments and as such humic-based reactions pertinent to permeable reactive barriers, *in situ* flushing, bioremediation, and phytoremediation are examined in detail. Finally, this chapter introduces the novel concept of “designer humics” which are a special class of customized humics of the reduced structural heterogeneity and of the controlled size. They are developed and deployed to carry out one or more of the above *in situ* functions in an optimum manner and for the purpose of enhancing the efficacy of one or more remediation technologies. Designer humics possess specified reactive properties obtained by chemical modification and cross-linking of the humic backbone. This new class of reactive agents portend new opportunities for achieving enhanced remediation and for quantifying remediation performance. The latter is described in the context of the passive flux meter technology developed for direct measuring fluxes of contaminants and biomass.

1. Introduction

Effective remediation of polluted environments is one of the crucial issues on Agenda 21, which lists priorities for achieving sustainable development [1]. Eastern and Western

countries alike are currently facing environmental reclamation costs that are increasing exponentially. In the U.S. and Europe, remediation costs generally exceed the net economic value of the land, and often threaten responsible companies with bankruptcy. Given this perspective it is not surprising that scientists and engineers on both sides of the Atlantic have aggressively tried to develop novel technologies to meet regulatory standards at a fraction of the costs associated with traditional approaches (incineration, pump-and-treat, etc.) [2-7].

New remediation technologies are often discovered in process of overcoming limitations of current technologies, and *in situ* remediation is one novel class of technologies that shows considerable promise from both technical and economic perspectives [8-10]. *In situ* remediation relies upon natural and enhanced processes that govern the fate and transport of chemicals released in environment. To a large extent, the reliance on natural processes is predicated on a desire to control costs [11]. Thus, *in situ* technologies that deploy natural attenuating agents such as humic substances (HS) may be even more cost effective.

HS are ubiquitous in the environment and comprise the most abundant pool of non-living organic matter [12]. Their peculiar feature is polyfunctionality, which enables them to interact with both metal ions and organic chemicals. The palette of potential interactions includes ion exchange, complexation, redox transformations, hydrophobic bonding, etc. As a result, numerous studies have shown humics capable of altering both the chemical and the physical speciation of the ecotoxicants (ET) and in turn affecting their bioavailability and toxicity [13]. Hence, HS hold great promise functioning as amendments to mitigate the adverse impacts of ET and as active agents in remediation.

The goal of this chapter is to elucidate emerging concepts of HS-based remediation technologies. Thus, the objectives are: (1) to categorize the interactions encountered between humics, ecotoxicants and living organisms in a polluted environment in the context of remediation chemistry; (2) to assess the scope of current remedial applications of humics, and (3) to define promising directions of technological developments for remedial implementation of humics.

2. Basic definitions and main features of humic substances

2.1. GENESIS, SOURCES, AND RESERVES OF HUMIC SUBSTANCES IN THE ENVIRONMENT

Humification is the chemical-microbiological process of transforming debris from living organisms into a general class of refractory organic compounds otherwise known as humic substances. It is the second largest process after photosynthesis and involves 20 Gton C/a [12]. Humic substances account for 50 to 80% of the organic carbon of soil, natural water, and bottom sediments [14-16].

Humic materials are typically derived on an industrial scale from peat, sapropel, and coal. *Peat* is a heterogeneous mixture of more or less decomposed plant material

(humus) that accumulated in a water-saturated environment in the absence of oxygen [17]. *Coalification* of plant debris preserved in peat mires leads to the formation of *humic coals*. Terms like *peat*, *lignite*, *subbituminous*, *bituminous* and *anthracite* indicate different stages of the coalification process, and they also denote the rank of various coals. The term “*brown coal*” is often used for lignite and subbituminous coals, while “*hard coal*” indicates coals of higher rank. The net result of coalification is an extension of the humification process to include a continuous enrichment of fixed carbon with increasing rank. The relevant increments of carbon content, or % of the total mass, range from: 10-30 (peat), 30-40 (lignites), 40-65 (subbituminous), 65-80 (bituminous), and over 80 (anthracite) [18]. *Sapropel* is an unconsolidated sedimentary deposit rich in *bituminous* substances [19]. It is distinguished from peat in being rich in fatty and waxy substances and poor in cellulosic material. When consolidated into rock, sapropel becomes oil shale, bituminous shale, or *sapropelic* (boghead) *coal*.

The richest source of HS is *leonardite*, a soft brown coal-like deposit usually found in conjunction with deposits of lignite. Leonardite is the most widely used raw material for production of commercial humic preparations [20] followed by other low-rank coals, peat, and sapropel. Table 1 shows the reserves of inexpensive humics-rich materials are immense; however, these reserves are not currently being tapped for environmental remediation.

Table 1. Reserves of humic materials of industrial value.

Source	Amount, Gton C	Ref.
Lignite and Subbituminous coal (Total/Recovered)	1120/512	[21]
Anthracite and Bituminous coal (Total/Recovered)	3880/571	[21]
Peat	400-500	[22]
Sapropel	800	[23]

2.2. CLASSIFICATION, STRUCTURE AND REACTIVITY OF HUMIC SUBSTANCES

Being the products of stochastic synthesis, HS have an elemental composition that is non-stoichiometric, and structure which is irregular and heterogeneous [24]. Aiken et al. [14] defined HS as “a general category of naturally occurring, biogenic, heterogeneous organic substances generally characterized as yellow to black in colour, of high molecular weight, and refractory”. MacCarthy and Rice [25] hypothesized that the structural heterogeneity of humics may explain their resistance to biodegradation as longevity of HS in soils is typically on the order of thousands of years. The recalcitrant nature of humics is of practical relevance particularly when the objective is to develop soil/aquifer remediation technologies predicated on a reactive matrix that is not consumed by microorganisms during remediation.

The best illustration of the stochastic nature of HS is provided by the structural model of Kleinhempel (1970) [26] depicted in Figure 1. Clearly, as shown in this figure, a single structural formula cannot be ascribed to any humic sample; consequently, current definitions and classifications of HS are based on isolation procedures rather than on specific molecular features. Thus, the most commonly applied classification is based on humic constituent solubility in dilute acids and bases [27]: *humic acids (HA)* represent the fraction that is insoluble at $\text{pH} < 2$, *fulvic acids (FA)* constitute the fraction soluble under all pH conditions, and *humins* is the fraction insoluble under all pH conditions. Alkali extraction is the most common industrial technique of preparing humics from brown coal or peat and the resultant salts of humic acids are called *humates*. Humates of sodium, potassium, and ammonium comprise the major fraction of the commercially available humic products. The term “humates” is often used to designate any commercially available humic-based product; however, in this chapter, the term is used only to designate the alkali/alkali-earth metals or ammonium salts of HA.

Despite its stochastic nature, HS from different sources share common elements of structural organization. The average humic macromolecule consists of a hydrophobic aromatic core that is highly substituted with functional groups (mostly carboxyl and hydroxyl), and with side aliphatic chains. The core is ensconced in a periphery of hydrolysable carbohydrate-protein fragments [15, 28]. The mass fraction of peripheral fragments decreases with humification; hence, the contribution of labile fragments is greatest among humics derived from composts followed by peat, soil, and finally coal. Coal-derived humics are enriched in condensed aromatic structures and depleted in aliphatic carbohydrate moieties; thus, these humics are much more hydrophobic and less biodegradable than their peat-based counterparts.

The structural complexity inherent in HS creates opportunities for a broad range of chemical interactions as indicated in Figure 2. Humics can be oxidized by strong oxidants; act as reducing agents; take part in protolytic, ion exchange, and complexation reactions; participate in donor-acceptor interactions; engage in hydrogen bonding; and take part in van-der-Waals interactions [29 and citations in it]. Hence, HS can interact practically with all chemicals released in the environment. More pertinent, however, is that humics interact with all classes of ecotoxicants including: heavy metals, petroleum and chlorinated hydrocarbons, pesticides, nitroaromatic explosives, azo dyes, actinides, etc. as shown in Figure 3. Indeed, humics are known to form stable complexes with heavy metals [30-34] and adducts with hydrophobic organic compounds [35-38]; produce charge-transfer complexes [39, 40]; act as electron shuttles [41, 42] and mediate redox reactions of transition metals [43], of chlorinated and nitrated hydrocarbons [44, 45]; adsorb onto mineral surfaces [46, 47]; and influence the interphase distribution of the contaminants [48, 49]. Finally, humics can strengthen the resistance of living organisms against non-specific stress factors [50, 51].

This unique constellation of reactive features strongly suggests HS have the potential to address a broad spectrum of needs within the focus area of environmental remediation [53]. This theoretical statement is confirmed by multiple examples of actual applications in remediation [54-58]. However, to ensure optimum and systematic application, an expanded knowledge base is needed concerning interactions between humics, ecotoxicants, and living organisms.